

Outgassing Measurements for Three Materials, Combined with Vacuum Ultraviolet Radiation Illumination of the Volatile Condensable Materials

1.0 Introduction

The photolysis of three organic materials, by vacuum ultraviolet (VUV) radiation, has been quantified using 15-MHz temperature-controlled quartz microbalances (TQCM's). The rate at which molecular species, released from the individual samples, condensed on two TQCM's was measured for periods of up to 139.9-hours. The individual samples were heated in an effusion cell and the emitted molecular species collected on a pair of TQCM's which were maintained at -40 degrees Celsius.

At several points during the deposition measurement, the deposition surface of one TQCM was illuminated by a 30 Watt deuterium lamp, and the loss of material from that surface was observed. VUV illumination of the TQCM, concurrent with condensation, reduced the rate that material was lost from the deposition surface. These measurements present a contrasting picture of molecular deposition, in the presence of VUV, to that presented by other investigators (1,2) who observed an enhanced rate of molecular deposition, when the deposition surface was illuminated by VUV.

2.0 Facility Description

The vacuum chamber in which the deposition measurements were made is a glass bell jar that seals against the metal base of the chamber. The chamber can be evacuated to a

pressure of to 6.6×10^{-5} Pa (5×10^{-7} torr) or less by a turbomolecular vacuum pump. A liquid nitrogen reservoir in the chamber, that passively cools a large cold wall, provides some additional pumping capacity.

The sample is heated to the desired temperature in an effusion cell that has a direct "line of sight" to both of the chamber's two TQCM's. The axis of the effusion cell is at an angle of 25 degrees to the plane of the deposition surface of TQCM#1 and 41 degrees to the deposition surface of TQCM#2. The plane of the deposition surface of TQCM#2 is rotated 12-degrees from the line of sight from the effusion cell. The distance from the effusion cell to TQCM#1 was typically 14.2-cm and 13.8-cm to TQCM#2.

A 30-Watt deuterium lamp is located 36.5-cm from TQCM#1 and the axis of the lamp is aligned with the normal, of the deposition surface, of TQCM#1. There is no direct line of sight from the UV lamp to TQCM#2 but some VUV radiation does reach this TQCM, possibly scattered from hardware surfaces in the chamber. VUV illumination of the deposition surfaces of the TQCM's did not alter the performance of either microbalance. The spectrum of the lamp (Fig. 1) contains a Lyman Alpha band in addition to very intense peaks at 156 nm, 159 nm, and 161 nm.

Both the Effusion cell and the VUV lamp have shutters that block the line of sight between each of them and the TQCM's. The efficiency of the effusion cell shutter varies between 33 and 88 percent, as measured by TQCM#1, and the efficiency appears to decrease as the deposition rate decreases.

Figure 1 A vendor provide spectrum for the 30-Watt deuterium lamp.

Both TQCM's are mounted in copper blocks that act as heat sinks for the sensors.

Provisions have been made for mounting witness coupons on these blocks, adjacent to the TQCM's, for the collection of samples for ex-situ chemical analysis and optical measurements.

3.0 Measurement Description

The deposition measurements were based on the American Society for Testing and Materials, Method E-1559 (3), which is commonly used to quantify the rate at which molecular species, emitted from an effusion cell, deposit on the surface of a quartz crystal microbalance. Several times during the deposition measurements, the deposition surface of TQCM#1 would be illuminated by the deuterium lamp, changing the rate at which the deposition process progressed. Once the effect of the VUV radiation had been observed, the lamp would be switched off and the "normal" deposition process resumed.

A sequence of operations for the VUV illumination of TQCM#1 was developed that addressed the less than 100 percent efficiency of the effusion Cell shutter.

Figure 2 illustrates the operation of the Effusion Cell and UV lamp shutters in support of the measurements presented in this paper.

Figure 2 A typical frequency curve showing the effects of operating the Effusion Cell Shutter, UV Lamp Shutter, and VUV illumination of the TQCM deposition surface.

From point A to point B, in Figure 2, the Effusion Cell Shutter is open and a clear “line of sight” exists between the Effusion Cell and the TQCM’s. From point B to point C the Effusion Cell Shutter is in the closed position, interrupting the “line of sight” movement of emitted species from the Effusion Cell to the deposition surfaces of the TQCM’s.

From point C to point D the Effusion Cell Shutter is again in the open position. From point D to point E the Effusion Cell Shutter is in the closed position, the UV lamp is on and the UV lamp Shutter is not blocking the UV lamp’s illumination of TQCM#1. From point E to point F the Effusion Cell Shutter is in the open position as is the UV lamp Shutter. From point F to point G the Effusion Cell Shutter is in the open position and the UV lamp Shutter is closed, blocking the light emitted by the VUV lamp.

The effects of solar illumination of TQCM’s were previously investigated, for the Space Shuttle Program (4), in support of the post-flight analysis of TQCM measurements that were part of the Evaluation of Oxygen Interaction with Materials flight experiment. Two separate effects were observed during the first 100 to 200-seconds of illumination of the microbalance crystal with a radiance of 135-mW/cm².

There was an initial, linear decrease in the beat frequency attributed to expansion of the TQCM’s quartz crystals, altering the piezoelectric spring constant of the crystals, during the first 5 to 10-seconds of the illumination. This is followed by a quickly decaying, asymptotic decrease in the beat frequency that was attributed to radiative heating of the crystal and the material deposited on the crystal.

Six TQCM’s were included in the earlier TQCM solar illumination, stability study and in each case the initial, linear mass loss occurred during the first ten seconds of

illumination; irregardless of the temperature of the deposition surface. During the illumination of TQCM#1 by the deuterium lamp, with the temperature-control circuit of the microbalance disabled, a short duration linear decrease in the beat frequency was observed. However, the decrease was observed seventy seconds after the illumination of the deposition surface (Fig. 3), suggesting that a thermal stability effect was observed rather than change in the mechanical properties of the quartz crystals.

Continued monitoring of the beat frequency recorded a continued loss of mass from the deposition surface followed by a mass gain (Fig. 4), as the temperature of TQCM#1 drifted from 16 degrees Celsius to 13 degrees Celsius (Fig. 5).

Since VUV illumination of the microbalance did not grossly affect the functional stability of the balance, no adjustments to the following deposition measurements were made.

Figure 3 The delay between the illumination of the TQCM deposition surface (shutter opening) and a decrease in the beat frequency occurred at approximately 1.3 hours. The data points were recorded at 10-second intervals. The horizontal line is the output from a photodiode mounted on the lamp side of the shutter. Opening the shutter moves the photodiode from in front of the UV lamp.

Figure 4 The overall effect of VUV illumination of the TQCM#1 during 1.45-hours of exposure.

Figure 5 Illumination of the TQCM deposition surface did not result in a heating of that surface. The TQCM temperature control was disabled for this observation period and the

temperature of the TQCM was dropping to the temperature of the copper mounting block, about 7 degrees Celsius.

4.0 Adipic Acid Measurements

To confirm the geometric relationship between the Effusion Cell and the TQCM's, deposition measurements were made with adipic acid (Chemical Abstracts Service Registry Number 124-04-9). The deposition data collected was then used to calculate the enthalpy of sublimation, at several Effusion Cell temperatures, of the adipic acid. Good agreement of the calculated enthalpy of sublimation with previously published values for this quantity, confirmed that the system was performing as designed and the relationship of the Effusion Cell to the TQCM's is understood (5).

Figures 6 and 7 show the Adipic Acid measurements made over an Effusion Cell temperature range of 24 to 58 degrees Celsius and condensed on a -40 degree Celsius surface.

Figure 6 Adipic Acid measurements for TQCM#1. Points falling on the "hand drawn" line would have a 100-percent agreement with the published values for the enthalpy of sublimation. Some percentages are indicated to illustrate the agreement of the calculated heat of enthalpy for these measurements with the published value.

Figure 7 Adipic Acid measurements made with TQCM#2. As in Figure 6, data points falling on and near the “hand drawn” line have a high degree of correlation to the published value for the enthalpy of sublimation for this material.

Closing and opening the Effusion cell Shutter modified the rate at which material was deposited on the TQCM's. VUV Illumination of the deposition surface, while the Effusion Cell Shutter was in the closed position resulted in a loss of material from the TQCM deposition surface. Opening the Effusion Cell Shutter, while the deposition surface was illuminated with VUV, reduced the rate of loss (Fig.s 8 and 9).

The loss of material was clearly observed during a total of six VUV exposures or illuminations of the deposited material (Table 1). Interaction of the VUV with material emitted from the effusion cell, but not yet in contact with the deposition surfaces, was also possible but not addressed by these measurements.

Figure 8 A typical frequency curve observed during shutter operations and VUV illumination of TQCM#1. The effect of opening the effusion cell shutter (2.95-hours) is not apparent in this figure.

Figure 9 Shutter operation and VUV illumination of TQCM#2. The effect of opening the effusion cell shutter (2.95-hours) had a clearly discernable effect.

Table 1

		TQCM#1			
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Effusion Cell Temperature	No Illumination	No Illumination	No Illumination	VUV Illumination	VUV Illumination
Degree Celsius	Shutter Open	Shutter Closed	Shutter Open	Shutter Closed	Shutter Open
	Hz/hour	Hz/hour	Hz/hour	Hz/hour	Hz/hour
32	49.123	25.538	28.121	-193.3	-79.228
39	26.443	13.857	28.216	-384.48	-91.757
40	31.578	16.414	30.738	-465.92	-163.63
45	43.93	20.945	58.032	-253.63	-88.899
50	105.78	29.681	114.32	-520.48	-427.64
56	180.97	37.082	254.87	-782.96	*-91.9024

*Second order polynomial fit of the recorded data with a 0.9952 correlation coefficient.

5.0 Zinc Selenium (ZnSe) Witness Plates

To augment the TQCM deposition measurements, one inch diameter ZnSe disks were positioned adjacent to both TQCM's for the collection of samples that would be analyzed by Fourier transform Infrared spectroscopy. The ZnSe disks were attached directly to the TQCM mounts, 0.5-inch thick copper blocks, which are actively cooled by a circulating water/glycol mixture. The temperature of the copper mounting blocks is about 7 degrees Celsius and it was assumed that the ZnSe disks were passively cooled to the same

temperature. Figures 10 and 11 are examples of the spectra from ZnSe disks, mounted around TQCM#1, during Scotch Weld 3501 Epoxy and S-383 Silicone Rubber deposition measurements.

To insure that material emitted by the samples would condense on the ZnSe disks, the outgassing from samples of Scotch Weld 3501 and S-383 Silicone Rubber were individually measured in the MSFC E-1559 Outgassing Facility. Deposition measurements are made in this facility using four cryogenic, quartz crystal microbalances that view an effusion cell. The temperature of one of the balances would be maintained at 10 degrees Celsius and the temperature of another microbalance would be maintained at -40 degrees Celsius to mimic the TQCM temperatures used for the Photo-deposition Facility measurements. Based on the deposition rates for the 10 degree Celsius microbalance, the effusion cell temperatures for the Scotch Weld 3501 and S-383 measurements, to be made in the Photo-deposition Facility, were selected.

Figure 10 An infrared spectrum of materials deposited on ZnSe disks during the Scotch Weld 3501 Epoxy, outgassing measurement.

Figure 11 An infrared spectrum of material deposited on a ZnSe disk during the S-383 Silicone Rubber, outgassing measurement.

6.0 Scotch Weld 3501 and S-383 Silicone Rubber Deposition Measurements

The Adipic acid measurements were typically made over a period of 24-hours, at a single Effusion Cell Temperature, and then Effusion Cell temperature would be increased for the next measurement. The Scotch Weld 3501 Epoxy and the S-383 Silicone rubber measurements were isothermal and much longer in duration than the individual Adipic Acid measurements.

Typically the Scotch Weld 3501 Epoxy and S-383 Silicone Rubber data files were about 24-hours in length and when all of the measurements were completed, the data files were appended together to create an overall picture of the outgassing measurement. The following frequency curves were constructed from multiple data files and some irregularities from the data file, appending process can be seen in the frequency plots for the overall measurement.

During these measurements the TQCM's were "baked out" when the amount of deposited material reaches the capacity of the microbalance which also contributed to the irregularities of the appended files. The deposited material is thermally driven from the deposition surface by raising the temperature of the TQCM's to 90-degrees Celsius, causing the deposited material to sublime from the deposition surface. The deposition surface was then cooled to -40 degrees Celsius and the deposition measurement resumed.

6.1 Scotch Weld 3501 Measurements

Unlike the Adipic Acid measurements, the Scotch Weld 3501 outgassing measurement was an isothermal measurement. The effusion cell temperature was 126-degrees Celsius and the TQCM deposition surfaces were held at -40 degree Celsius during the measurement. The duration of the measurement was 118.52-hours which started when

the sample reach the desire temperature for the measurement and includes the any periods when the TQCM's were "baked out".

The frequency curves for the overall deposition measurements are presented in Figures 12 and 13. The frequency curve for a typical VUV exposure of the material deposited on the TQCM's are presented in Figure 14. The deposited material was exposed to VUV four times (Table 2) during the overall outgassing measurement of the Scotch Weld 3501 Epoxy. The order of shutter operations, used during the VUV exposure of the Adipic Acid, was also used for these exposures and was presented in Figure 2.

Figure 12 The overall, TQCM#1, deposition measurement for Scotch Weld 3501 Epoxy.

Figure 13 The overall, TQCM#2, deposition measurement for Scotch Weld 3501 Epoxy.

Figure 14 the effects of Effusion Cell Shutter operations and VUV exposure can be clearly seen at 3.26-hours.

Table 2

	TQCM#1			
No Illumination	No Illumination	No Illumination	VUV Illumination	VUV Illumination
Shutter Open	Shutter Closed	Shutter Open	Shutter Closed	Shutter Open

Hz/hour	Hz/hour	Hz/hour	Hz/hour	Hz/hour
430.02	51.962	426.73	-174.36	252.14
378.17	*51.962	-----	-336.61	56.29
277.78	40.234	264.47	-192.31	112.67
173.83	27.634	167.8	-147.68	30.918

* The deposition rate with the Effusion Cell Shutter closed, and no VUV illumination, was not repeated before the second reported measurement was made, 3.5 hours after the first series of shutter operations and measurements.

6.2 S-383 Silicone Rubber

Like the Scotch Weld 3501 outgassing measurement, this 139.9-hour measurement was an isothermal measurement. The effusion cell temperature was 133-degrees Celsius and both TQCM's were maintained at -40 degrees Celsius, excluding TQCM baked out periods. Figures 15 and 16 show the overall frequency curves for the S-383 measurements. Typical frequency curves for the VUV exposure periods are presented in Figures 17 and 18 and the VUV exposures followed the order of operations previously used for the previous samples. There were a total of three VUV exposure periods (Table 3) during the overall S-383 measurement.

Figure 15 The overall frequency curve for TQCM#1.

Figure 16 The overall frequency curve for TQCM#2.

Figure 17 During the VUV illumination of TQCM#1 the Effusion Cell Shutter was opened at 24.18-hours.

Figure 18 The opening of the Effusion Cell Shutter at 24.8-hours had a more pronounced effect on TQCM#2.

Table 3

	TQCM#1			
No Illumination	No Illumination	No Illumination	VUV Illumination	VUV Illumination
Shutter Open	Shutter Closed	Shutter Open	Shutter Closed	Shutter Open
Hz/hour	Hz/hour	Hz/hour	Hz/hour	Hz/hour
56.227	12.657	52.078	-407.64	-99.823
37.106	13.518	43.018	*	4.6267
19.412	6.478	20.038	-68.914	-13.267

*The rate of change was not linear but the overall change in frequency was -36.598 Hz in 1.041 hours or a -35.156 Hz/hour loss.

7.0 Conclusions

Outgassing measurements for samples of adipic acid, Scotch Weld 3501 Epoxy, and S-383 Silicone Rubber, made in the Marshall Space Flight Center Photo-deposition Facility, produced results similar to outgassing measurements made in other facilities that are operated according to the ASTM E-1559 methodology. The efficiency of the Effusion Cell Shutter, in blocking the emission of materials from the Effusion Cell, was less than 100 percent and an order of shutter operations was adopted to address this inefficiency. Samples suitable for Fourier transform infrared analysis were successfully collected on passively cooled witness plates during the epoxy and silicone rubber outgassing measurements.

VUV illumination of material on the TQCM deposition surface resulted in the loss of material from that surface. The process involved is believed to be photolysis, and due to the inefficiency of the Effusion Cell Shutter, possibly occurring to a greater extent than recorded by these measurements. These measurements did not address the possibility that materials in transit, from the effusion cell to the TQCM, may have been altered by VUV illumination. Reactive molecular species, ions or free radicals, could have played a role in the observed loss, by a mechanism other than or in concert with photolysis of the deposited materials.

Direct illumination of the deposition surface, while the Effusion Cell Shutter was not in the "line of sight path" between the Effusion Cell and the deposition surface, reduced the rate at which material was lost from the TQCM. During the adipic acid,

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Scotch Weld 3501 Epoxy, and S-383 Silicone Rubber deposition measurements, the rate less than the deposition rate measured when the deposition surface was not illumination.

The deposition measurements reported here, document that VUV illumination of material condensing on a surface will not always occur at a rate greater than deposition rates measured without VUV illumination.

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9.0 References

1. Hall, D. F.; and Stewart, T. B.: "Photo-Enhanced Spacecraft Contamination Deposition," AIAA Paper 85-0953, 20th Thermophysics Conference, Williamsburg, VA, June (1985)
2. Tribble, A. C.: The Space Environment, Implications for Spacecraft Design Princeton University Press, Princeton, NJ, p 39, 1995
3. "Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials", in Annual Book of ASTM Standards, Vol. 15.03, American Society for Testing and Materials, Philadelphia, PA. P.9, 1993
4. Shuttle TQCM Calibration, Engineering report FAR-015-82 prepared by Faraday Laboratories, Inc., August 23, 1982, Contract NAS-8-34993
5. Albyn, K. C., "Quartz Crystal Microbalance Operation and In Situ Calibration", NASA/TM-2004-213550, November 2004.

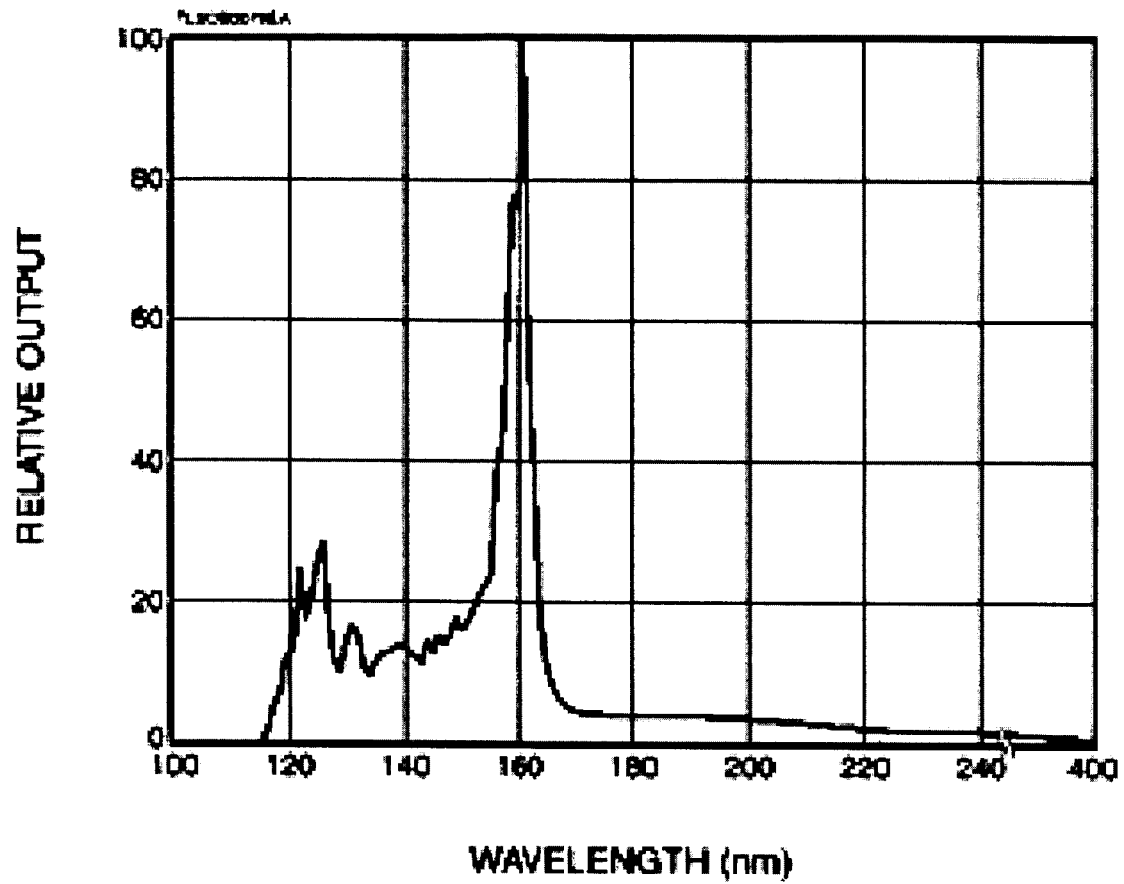


Figure 1 A vendor provide spectrum for the 30-Watt deuterium lamp.

Shutter and UV Lamp Operations

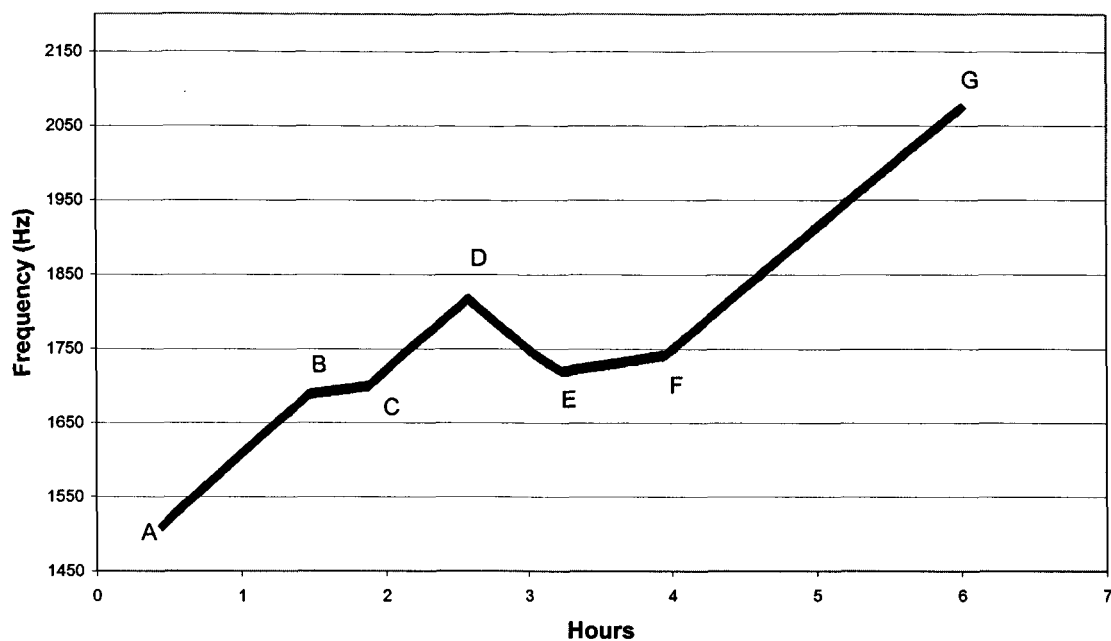


Figure 2 A typical frequency curve showing the effects of operating the Effusion Cell Shutter, UV Lamp Shutter, and VUV illumination of the TQCM deposition surface.

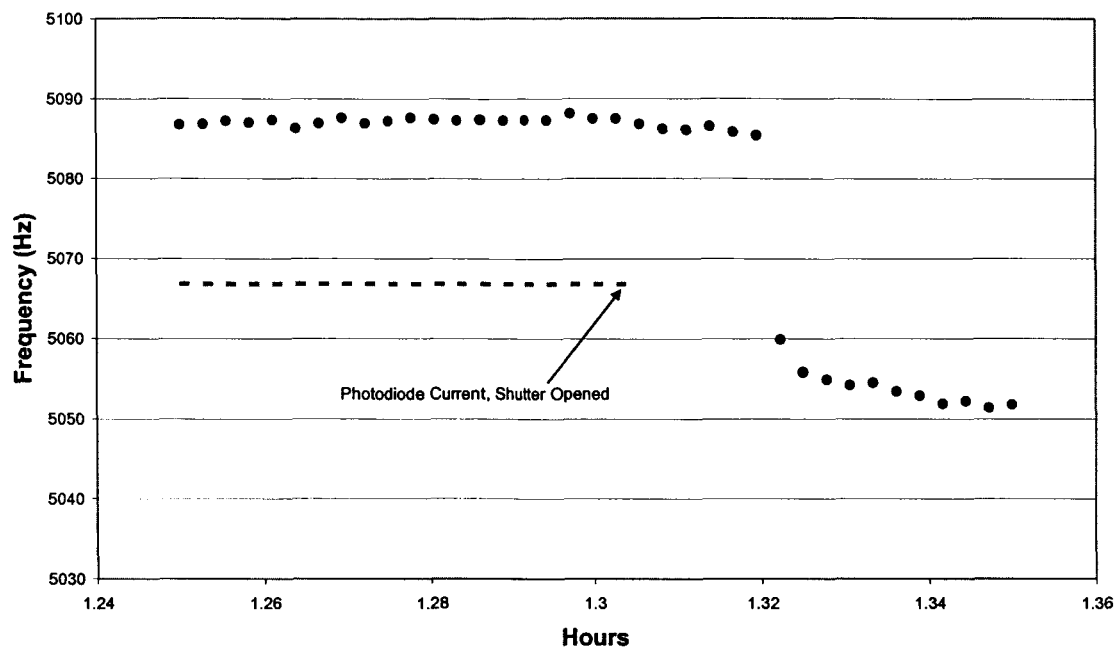
TQCM#1 PDApr0605

Figure 3 The delay between the illumination of the TQCM deposition surface (shutter opening) and a decrease in the beat frequency occurred at approximately 1.3 hours. The data points were recorded at 10-second intervals. The horizontal line is the output from a photodiode mounted on the lamp side of the shutter. Opening the shutter moves the photodiode from in front of the UV lamp.

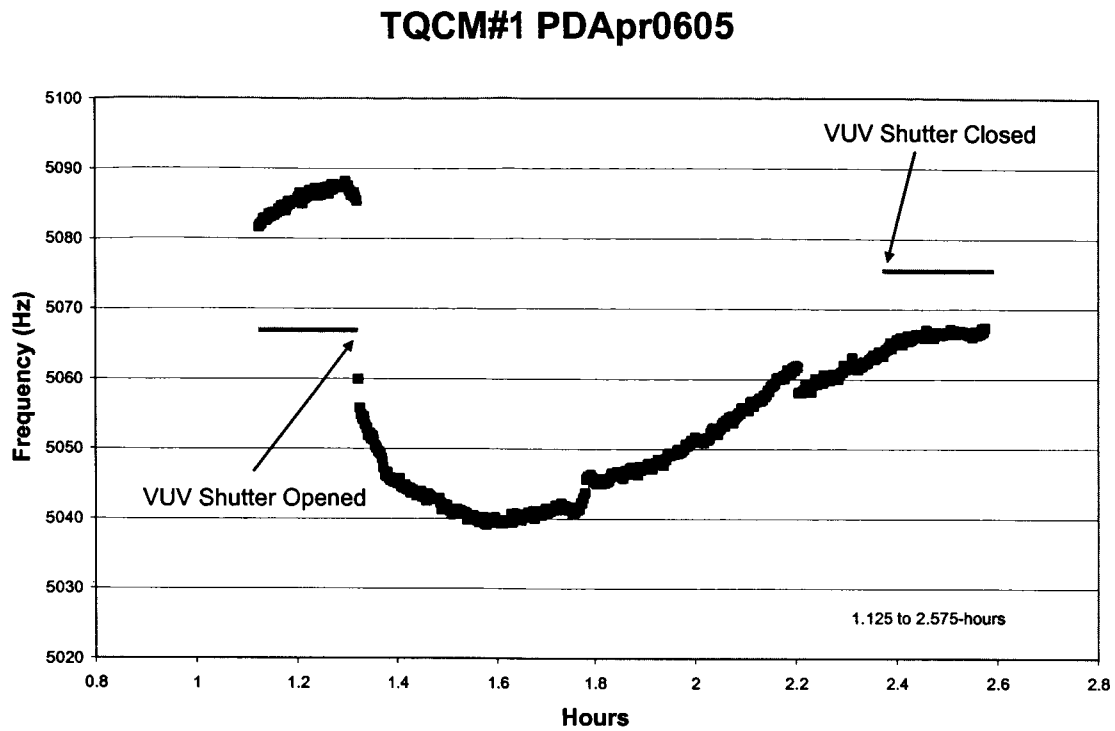


Figure 4 The overall effect of VUV illumination of the TQCM#1 during 1.45-hours of exposure.

PDApr0605 VUV Interaction with TQCM#1

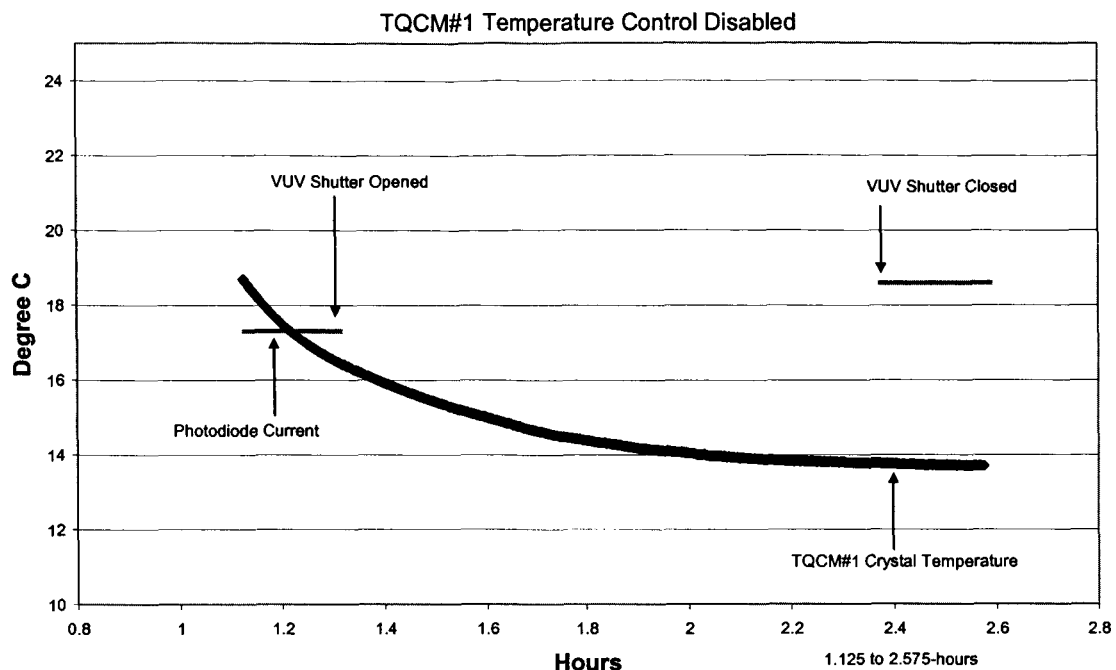


Figure 5 Illumination of the TQCM deposition surface did not result in a heating of that surface. The TQCM temperature control was disabled for this observation period and the temperature of the TQCM was dropping to the temperature of the copper mounting block, about 7 degrees Celsius.

TQCM#1 Adipic Acid - All Data

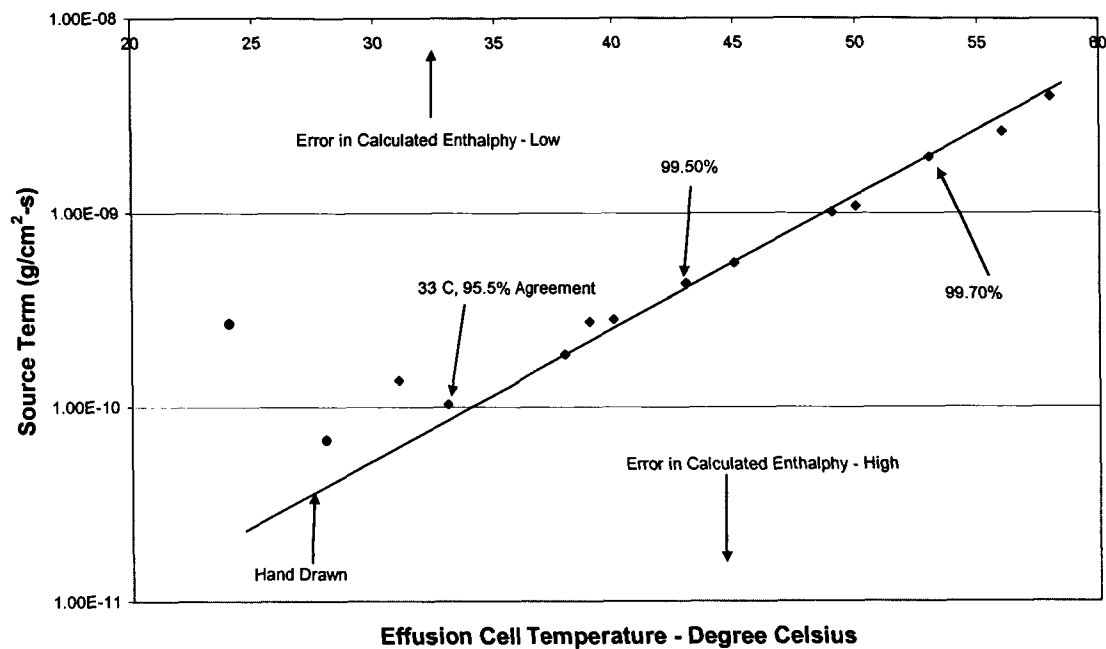


Figure 6 Adipic Acid measurements for TQCM#1. Points falling on the “hand drawn” line would have a 100-percent agreement with the published values for the enthalpy of sublimation. Some percentages are indicated to illustrate the agreement of the calculated heat of enthalphy for these measurements with the published value.

TQCM#2 Adipic Acid - All Data

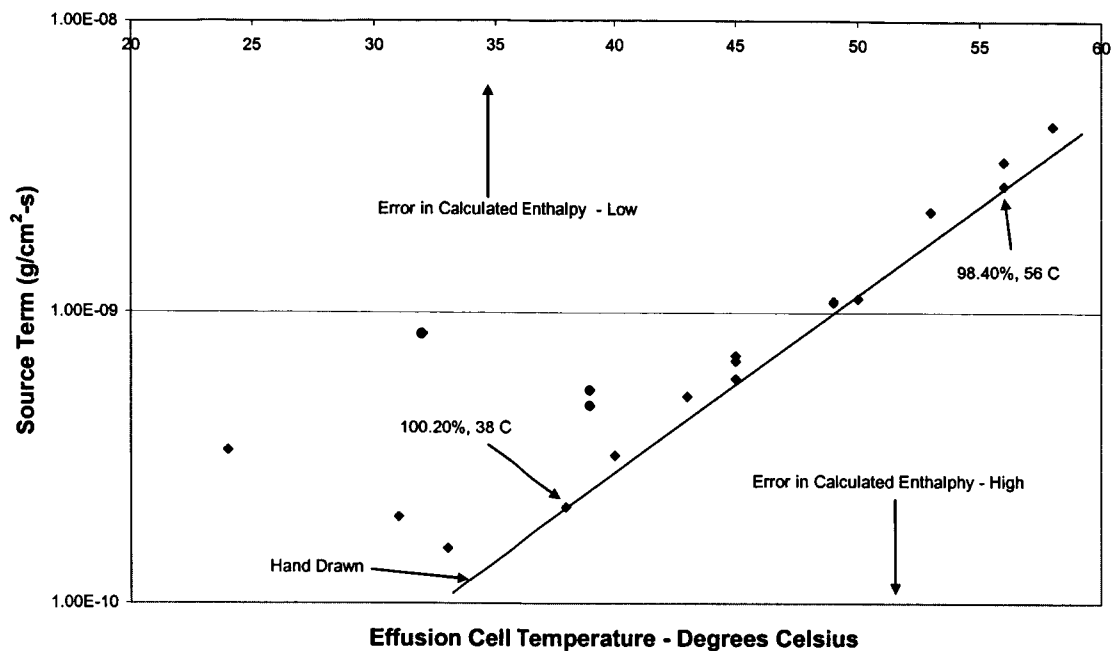


Figure 7 Adipic Acid measurements made with TQCM#2. As in Figure 6, data points falling on and near the “hand drawn” line have a high degree of correlation to the published value for the enthalpy of sublimation for this material.

Adipic Acid PDJun3005 TQCM#1

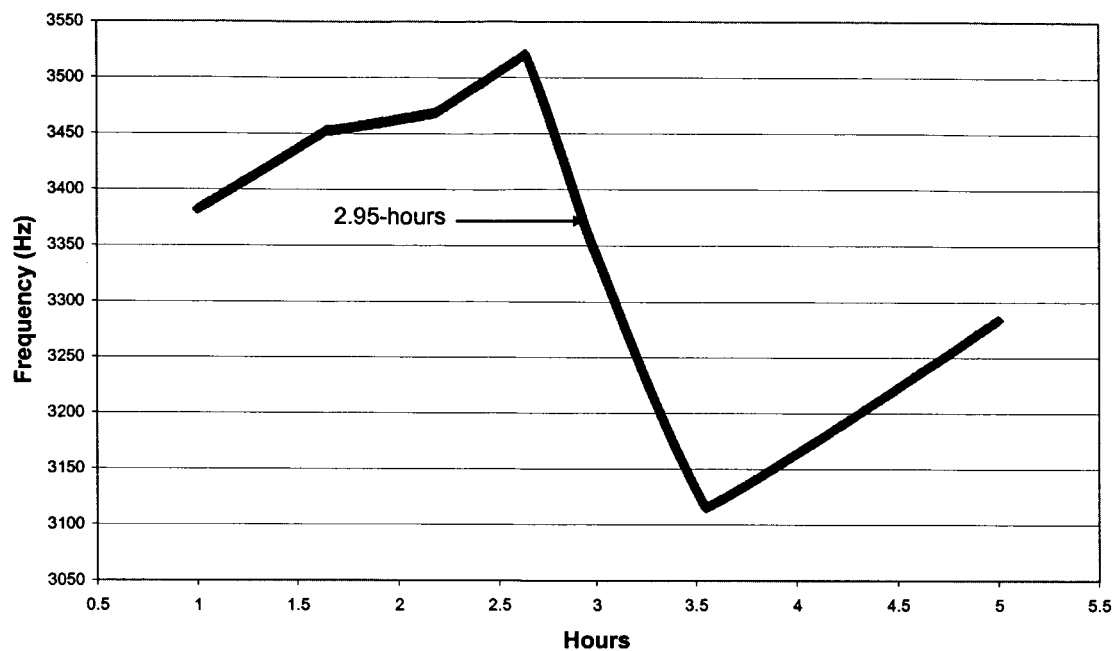


Figure 8 A typical frequency curve observed during shutter operations and VUV illumination of TQCM#1. The effect of opening the effusion cell shutter (2.95-hours) is not apparent in this figure.

Adipic Acid PDJun3005 TQCM#2

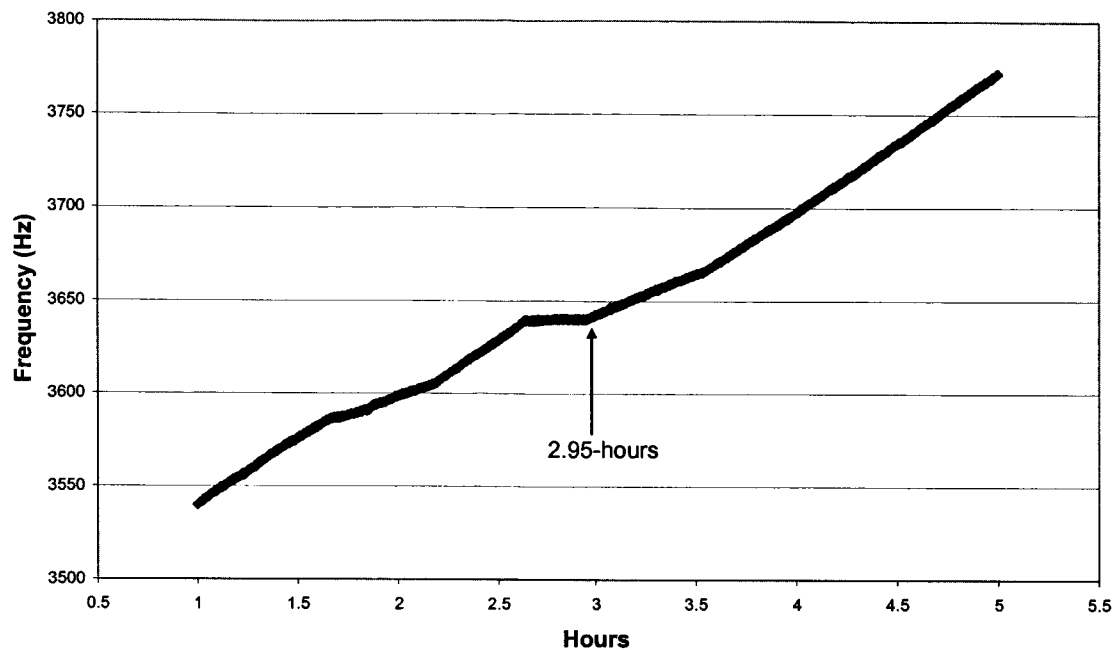


Figure 9 Shutter operation and VUV illumination of TQCM#2. The effect of opening the effusion cell shutter (2.95-hours) had a clearly discernable effect.

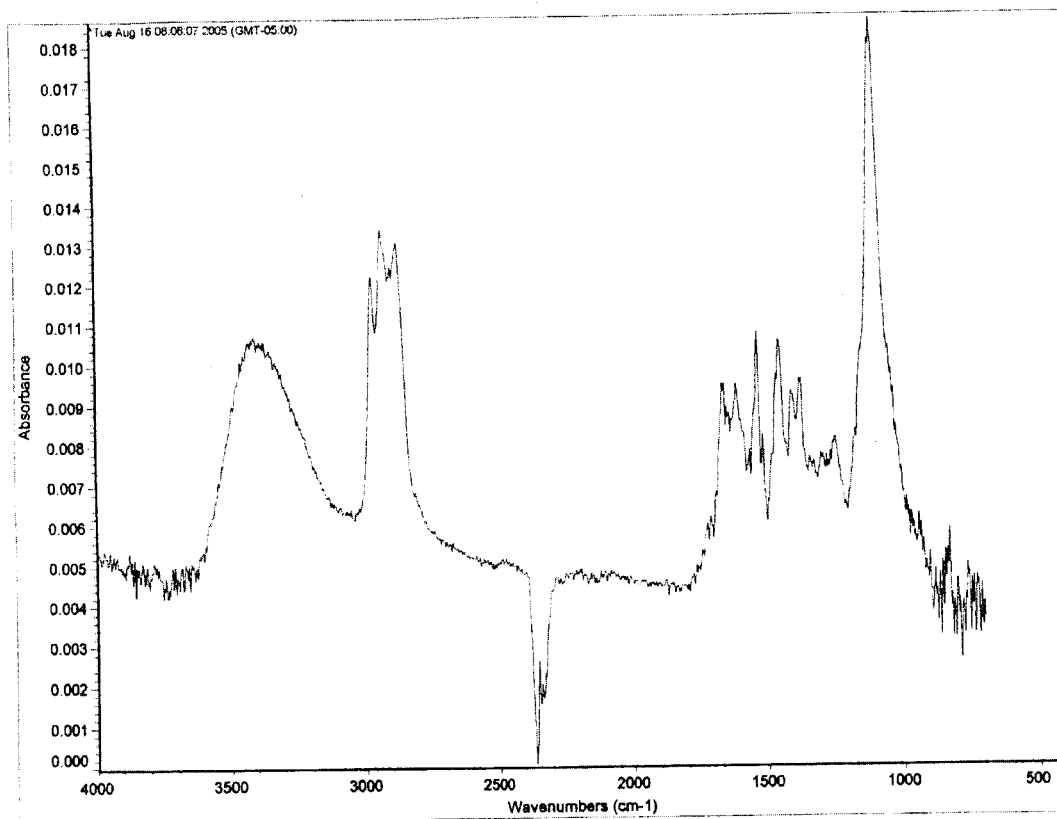


Figure 10 An infrared spectrum of materials deposited on ZnSe disks during the Scotch Weld 3501 Epoxy, outgassing measurement.

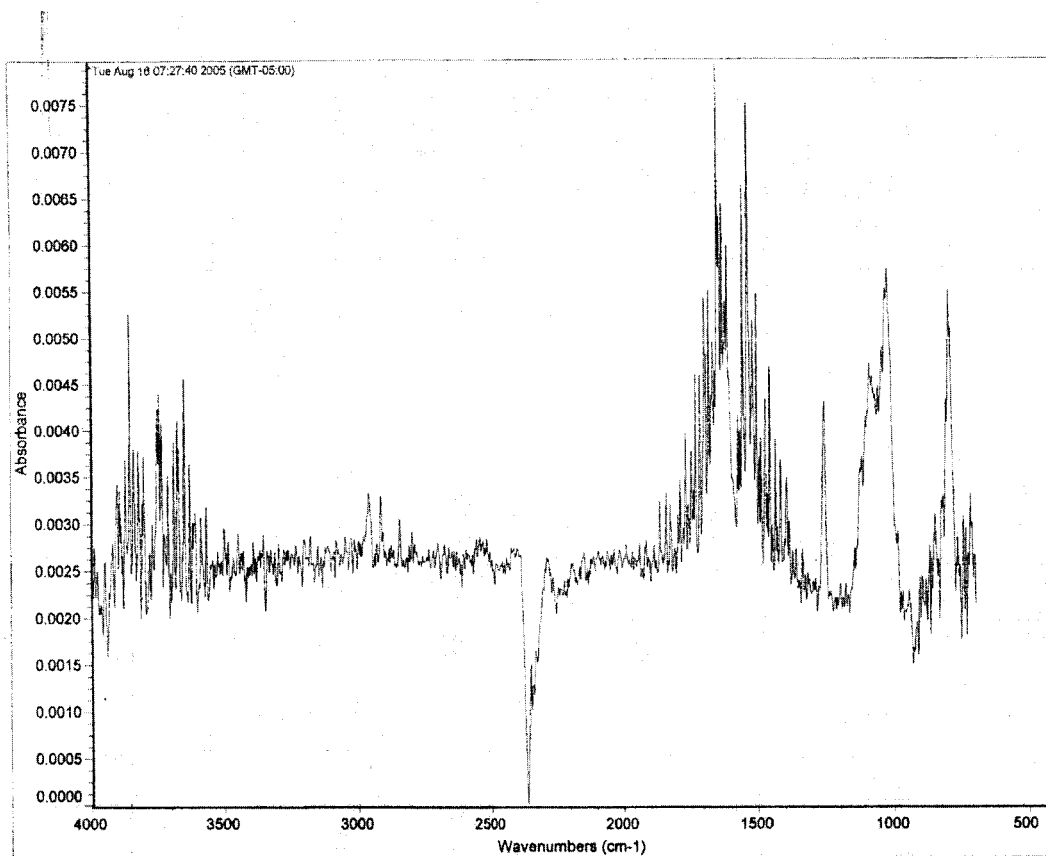


Figure 11 An infrared spectrum of material deposited on a ZnSe disk during the S-383 Silicone Rubber, outgassing measurement.

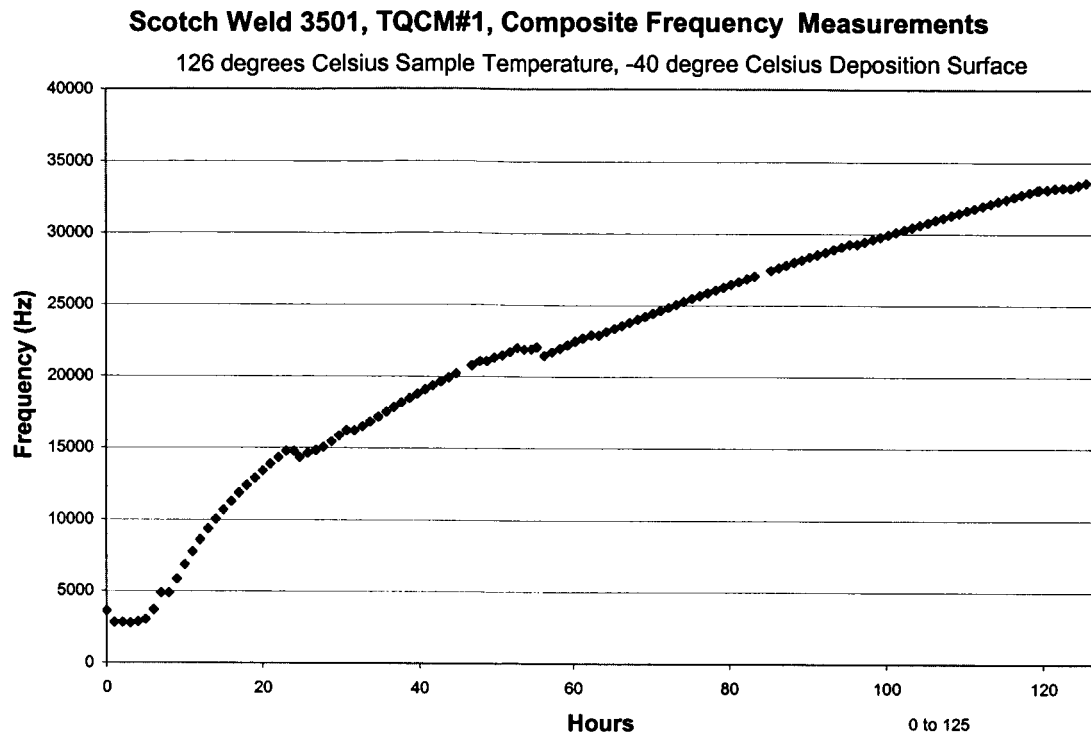


Figure 12 The overall, TQCM#1, deposition measurement for Scotch Weld 3501 Epoxy.

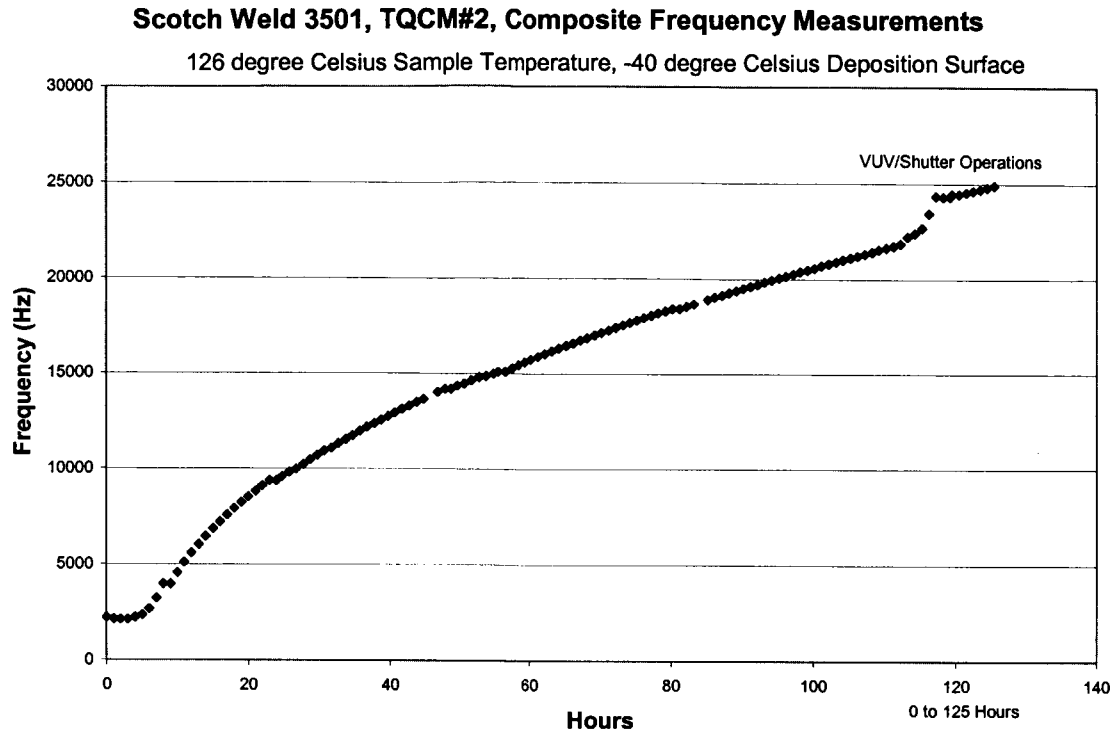


Figure 13 The overall, TQCM#2, deposition measurement for Scotch Weld 3501 Epoxy.

Scotch-Weld 3501 PDJul1805 TQCM#1

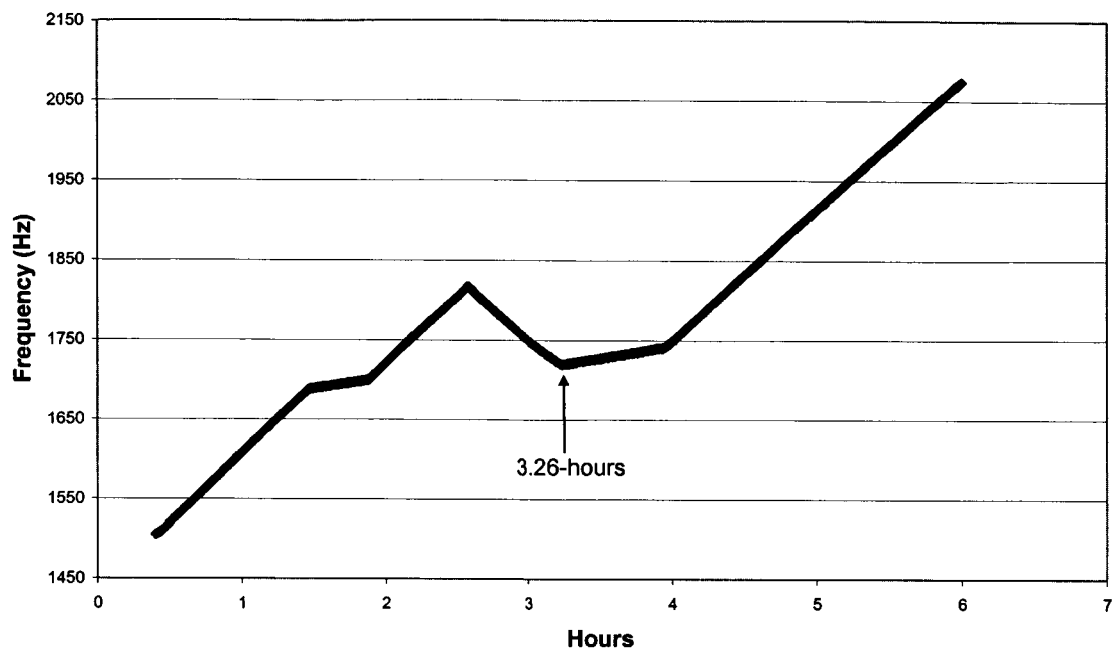


Figure 14 the effects of Effusion Cell Shutter operations and VUV exposure can be clearly seen at 3.26-hours.

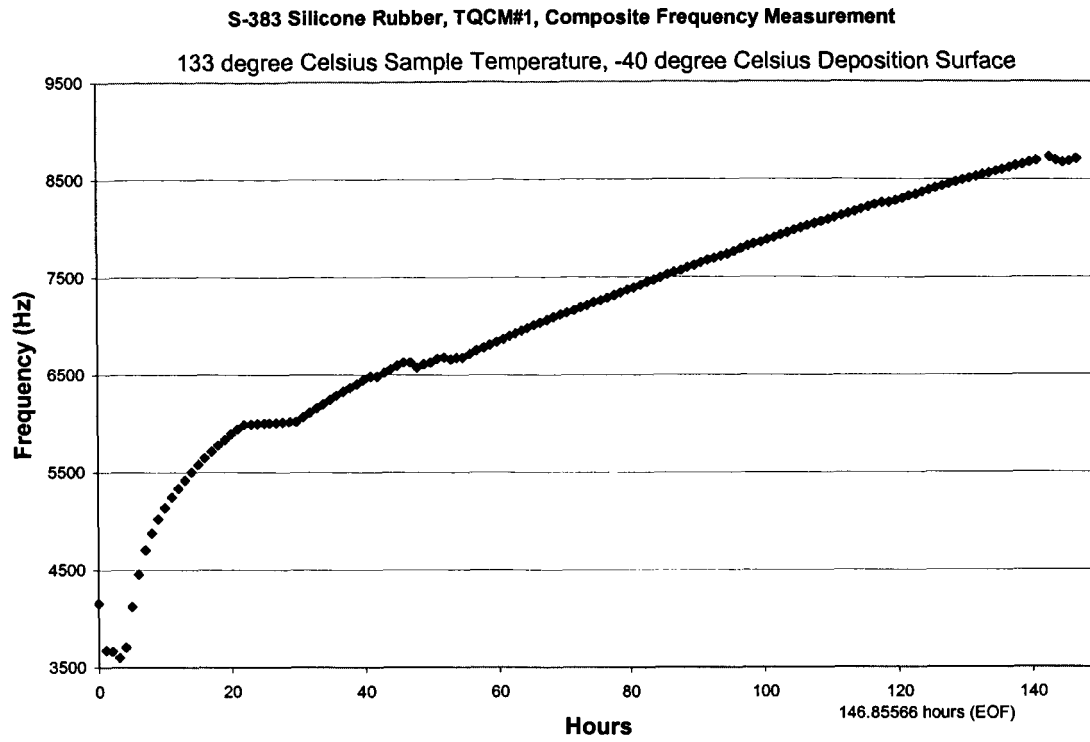


Figure 15 The overall frequency curve for TQCM#1.

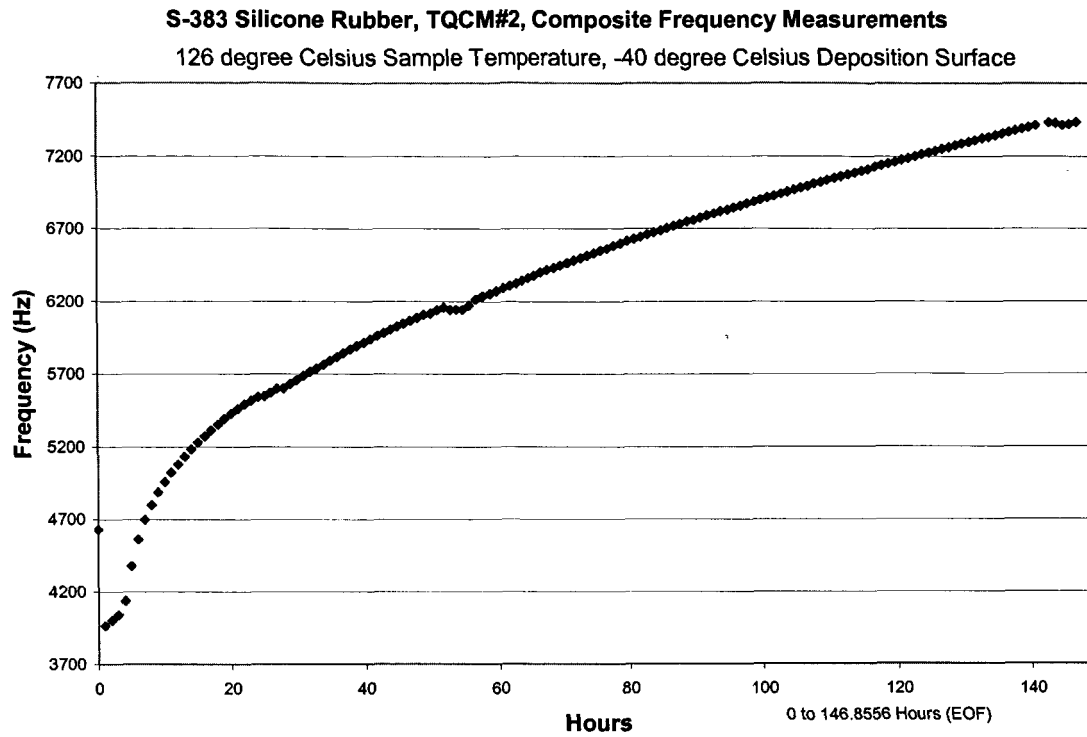


Figure 16 The overall frequency curve for TQCM#2.

S-383 Silicone Rubber PDJul2005 TQCM#1

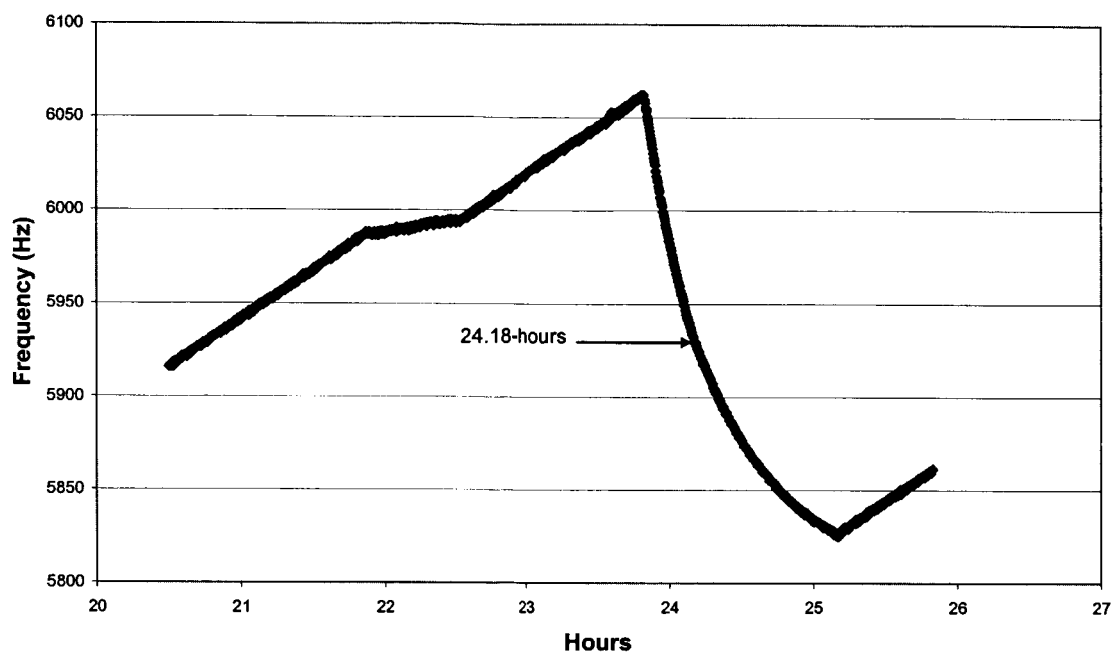


Figure 17 During the VUV illumination of TQCM#1 the Effusion Cell Shutter was opened at 24.18-hours.

S-383 Silicone Rubber PDJul2005 TQCM#2

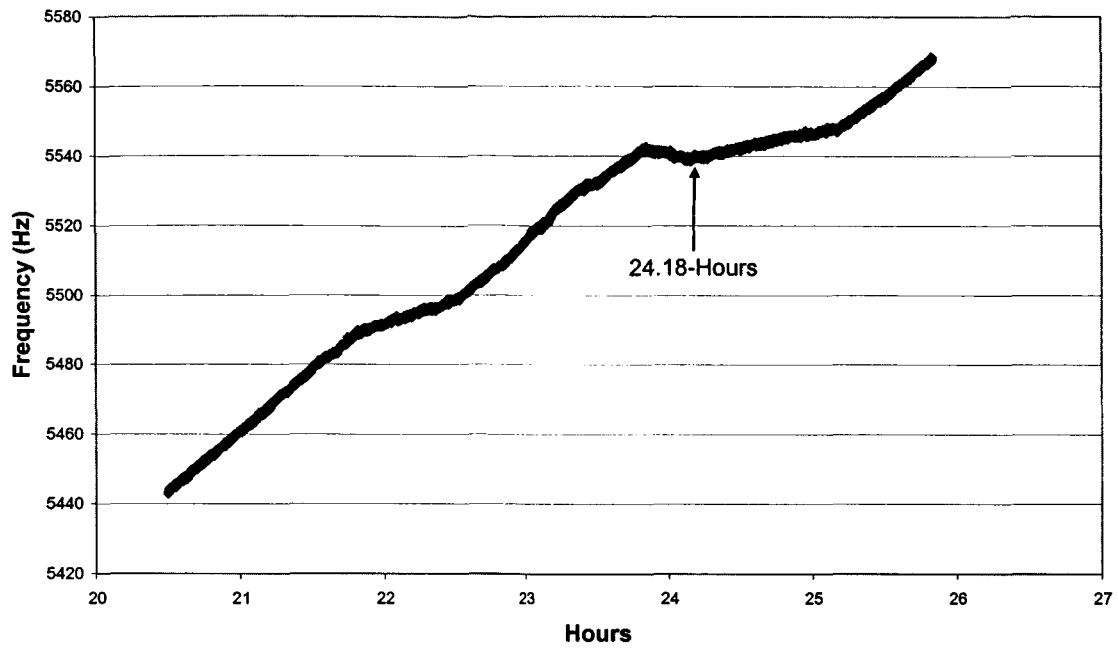


Figure 18 The opening of the Effusion Cell Shutter at 24.8-hours had a more pronounced effect on TQCM#2.